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Researching of dielectric membrane films obtained by reactive magnetron sputtering

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Abstract

The aim of the paper is the research of dielectric membrane films obtained by reactive magnetron sputtering. Simulation of temperature distribution on the membrane structures of different elemental composition in the process of heating and cooling was carried out. The manufacturing results and the results of the properties study of dielectric membrane films are presented. The qualitative analysis of membrane films stability to destruction and deformation in the process of heating and cooling is given. Optimum element compositions and formation modes of dielectric films for sensitive elements of semiconductor gas sensors are determined.

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Keywords: magnetron sputtering; dielectric membrane film; dielectric membrane structures; sensitive layer; sensitive element; gas sensor.

1. Introduction

One of the most important applications of MEMS – technologies is the formation of special platforms for sensitive layers of gas sensors – sensitive elements. Recently for analysis of gaseous environments are widely used semiconductor gas sensors. The measurements of gas concentration by such sensors accompanied by preheating of

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sensitive layers, selectively accelerates the processes on the surface and in the volume of the sensitive layers. The preheating of the sensitive layer improves such characteristics of gas sensors as sensitivity, selectivity, and speed of response. This is due to the obtaining of certain temperature ranges for measurement of gas concentration in which the molecules of the detectable gaseous have the greatest reactivity with the material of the sensitive layers. Heating temperature of sensitive layer for each combinations of sensitive layer material – detectable gas is individually defined and can reach 1000°C. On the possibility of achieving high temperature of sensitive layer has decisive impact its heat exchange with the environment through the construction of the sensitive element. Distinctive feature of sensitive element construction of such gas sensors is the heat insulating structure, also determines the power consumption of the sensor and the possibility of its long operation from the standalone power source (Sakai et al., 2001; Heule & Gauckler, 2003; Miasnikov et.al., 1991, Obvintseva, 2008; Bubnov et. al., 2008; Kozlov, 2006, 2008).

There are many different methods for heat insulating of sensitive layers, one of which is the using of hanging installation of sensitive elements on the wire in the case. This method differs by considerable heat dispersion through the construction of sensitive element because of its big sizes. Other heat insulating method of sensitive layers is the using of constructions on the basis of the suspended elements made in cavities of silicon substrates by the method of anisotropic etching of silicon. In this case it is difficult to combine with known technologies of sensitive layers formation and provides low heat insulating properties (Iovdalsky et. al., 1996). Sensitive elements based on membranes of porous silicon are suitable to formation by the group methods, but also provides low heat insulating properties (Maccagnani et. al., 1999). Sensitive elements based on membranes of porous aluminum oxide provides better heat insulating properties, but its production by the group methods is inapplicable (Gogish-Klushin et. al., 2010; Vasiliev et.al, 2006).

Dielectric membrane structures are the most perspective for using as the heat insulating constructions for sensitive elements of semiconductor gas sensors. It explains by the smallest coefficient of heat conductivity of dielectric films from all known materials used as the membranes. In different references reports that such membranes can be made of SiO₂, Si₃N₄ or consistently created SiO₂ and Si₃N₄ multilayered films (Heater et. al., 2003; Puigcorbe et. al., 2001; Guillemet et. al., 2000). The group technology of such sensitive elements formation is applicable, but its production is considerably complicated because of the fragility and complexity of element composition reproducibility of membranes, which has decisive impact on the final characteristics of the device. Therefore a large number of scientific works are devoted to development of manufacturing technologies for such sensitive elements.

The paper is devoted to researching of thin dielectric membrane films of different element composition obtained by the reactive magnetron sputtering of silicon in the environment of argon, nitrogen and oxygen. The aim of the work is the search of optimal element composition of dielectric films for production of sensitive elements by the method of two-stage unilateral anisotropic etching of silicon, which feature is the formation of membranes at the final stage of anisotropic etching of silicon, after the formation of sensitive layers, with their protection from the contact with etchant (Veselov et. al., 2011, 2012, 2013, 2015).

2. Simulation of temperature distribution on the membranes area

Simulation of temperature distribution on the area of silicon oxide and silicon nitride membranes and four-layer membrane (obtained by layers interleaving of silicon oxide and silicon nitride with the thickness of 0.5 μm) in the process of heating and cooling was carried out by means of program complex Synopsys TCAD. In simulation the thickness of the substrate was adopted equal to 10 μm, because the actual thickness of the substrate will sharply increases the simulation time, but on the final result of the simulation will not affects significantly. The membrane size was adopted equal 1 × 1 mm, the thickness of the membrane - 2 μm, the strip width of platinum resistive heater - 20 μm, the strip length of the heater - 2.95 mm, the calculated area of the heating region is about 0.30 mm², the strip thickness of the heater is 0.5 μm, the calculated resistance of the heater is about 31.5 Ω. Simulation of temperature distribution was carried out when filing to the resistive heater of rectangular pulse with voltage 0.9 V and duration 100 ms. Front time and fall time of the pulse is 10 ms. Total simulation time of the cycle of heating and cooling is amounted 210 ms. For membranes of different dielectric materials were obtained dependence for temperature against coordinates, with 0 in the center of the membranes, at the moment of the highest heating of membranes and dependence for temperature against time in the center of the membranes. For example, see Fig. 1, 2. Differences in maximum temperatures explained to the differences in thermal conductivity of the membranes material. Thus, membranes of silicon oxide have the best heat insulation properties, but membrane of silicon nitride

and four-layer membrane characterized by faster temperature stabilization, which will provide the quick output mode to the measurement temperature of gas concentration, which is their advantage.

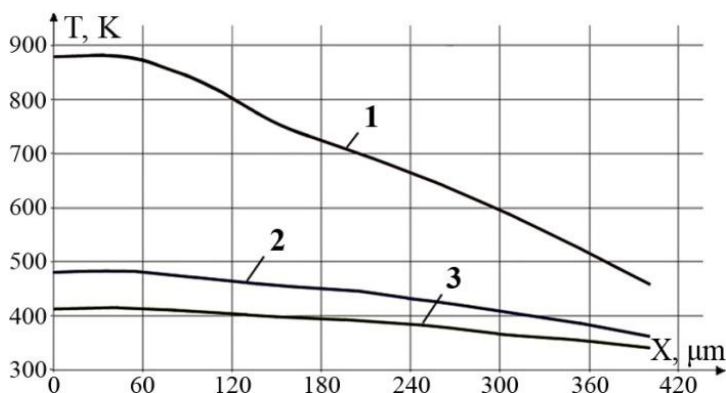


Fig. 1. Dependence for temperature against coordinate X , with 0 in the center of the membranes, at the moment of the highest heating of the membranes of: 1 - silicon oxide; 2 - four-layer membrane; 3 - silicon nitride.

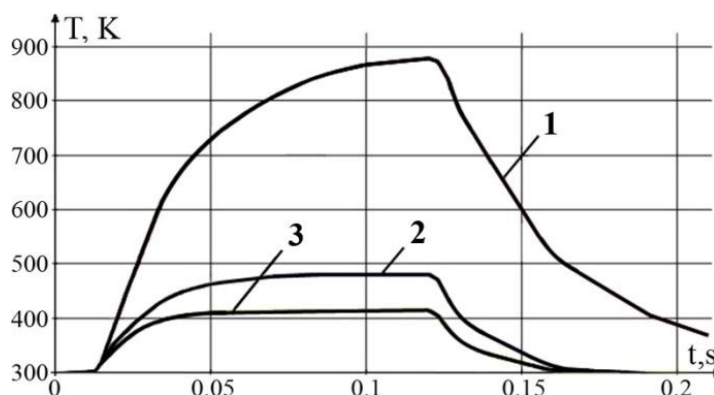


Fig. 2. Dependence for temperature against time in the center of the membranes of: 1 - silicon oxide; 2 - four-layer membrane; 3 - silicon nitride.

3. Formation and properties study of dielectric membrane films

As substrates for the formation of membrane films were selected silicon substrates with the diameter of 76 mm, with the thickness of $(380 \pm 20) \mu\text{m}$ and crystallographic orientation of (100). The formation of dielectric membrane films was carried out at the unit UVN-71PZ modified for reactive magnetron sputtering and equipped with three-channel gas injection system into the chamber. To remove contaminants from substrates surface before sputtering was carried out the washing in the heated peroxide-ammonia solution. Then, after loading of substrates into the working chamber and it's pumping, the chamber was filled by argon and was carried out the ion cleaning. Whereupon, the chamber was filled by argon, nitrogen and oxygen and was conducted reactive magnetron sputtering of membrane films on the thermal silicon oxide underlay. While the flow of argon was set as constant ($Q(\text{Ar}) = 1.2 \text{ l/h}$), the flows of oxygen and nitrogen were changing ($Q(\text{O}_2) = 0.2\text{-}1.4 \text{ l/h}$, $Q(\text{N}_2) = 1.2\text{-}3.6 \text{ l/h}$). The dielectric membrane films of different elemental composition were obtained.

The element composition study of obtained films was carried out by XPS (X-ray photoelectron spectroscopy by the electron spectrometer XSAM-800, the company Kratos). The study of the element composition was carried out on the surface and in the volume of obtained films. For layer-by-layer films analysis was carried out the ion etching in the environment of argon for 1-2 minutes. The results of the study are shown in table 1. Also, all samples were studied at adhesion level by method of the adhesive tape. Most films were characterized by good level of adhesion.

Table 1. Results of the element composition study of obtained dielectric films.

№	Film	Element composition, (%)					Element ratio*	Gas flow, (l/h)		
		Si	O	N	C	Mo		Ar	O ₂	N ₂
1	Surface	30	48	5	17	0	6:10:1	1.2	1.4	1.2
	Volume	38	50	4	7	1	10:13:1			
2	Surface	36	38	21	5	0	2:2:1	1.2	1.2	1.6
	Volume	43	35	17	4	1	3:2:1			
3	Surface	32	45	15	8	0	2:3:1	1.2	1.0	2.0
	Volume	37	37	12	14	0	3:3:1			
4	Surface	34	42	13	11	0	3:3:1	1.2	0.8	2.4
	Volume	41	37	12	9	1	3:3:1			
5	Surface	35	26	25	13	1	1:1:1	1.2	0.6	2.8
	Volume	47	19	26	5	3	2:1:1			
6	Surface	29	33	20	16	2	1:2:1	1.2	0.4	3.2
	Volume	34	28	22	13	3	2:1:1			
7	Surface	32	28	22	17	1	1:1:1	1.2	0.2	3.6
	Volume	42	22	29	5	2	2:1:1			

* values are rounded to integers.

The suitability of the obtained films for fabrication of membrane structures was determined by dint of detecting the mechanical stresses by visual control of membranes bending during the direct heating to high temperature and extracting substrates from the heated etchant at the formation of the membranes by anisotropic etching of silicon. Also, the dielectric membrane films were studied for resistance to etching in the organic alkaline etchant for the final stage of anisotropic etching of silicon [15]. Mass fractions of the etchant components: diaminoethane; pyrocatechol; water = 55%; 20%; 25% (density of the etchant at 20°C: $\rho = 1,055 \text{ g/cm}^3$). Dielectric membrane films were studied for resistance to etching in this solution by two ways:

Qualitative analysis. On the thermal silicon oxide underlayer were formed dielectric films on which were prepared metallization elements, which were coated by masking layer of the same dielectric material with the thickness of not exceeding 0.3 μm . Resulting samples were placed in the reservoir with etchant at 100°C and etched there for about of two hours. After that, samples were washed with deionized water with application of thorough wiping by wet cotton swab. If the changes of geometric dimensions of metallization elements were observed (partial exfoliation), it was indicated about etching of dielectric film, if it is not, was carried out next stage of the study.

Quantitative analysis. On the thermal silicon oxide underlayer were formed dielectric films with the thickness of not exceeding 0.3 μm . Resulting samples were placed in the reservoir with etchant at 100°C and etched there for about of two hours. Then, on the samples by lift off photolithography were formed strips of dielectric material with the thickness of about 10 μm . By this strips were determined residual thickness of the films and presence of it etching. It was made through the surface profile, obtained on the profilometer Dektak 150 company VEECO.

During the research of obtained films was revealed that the most suitable for production of dielectric membrane structures for sensitive elements of semiconductor gas sensors are silicon oxynitride films, which are shown in Table 1 under point 5, 6 and 7. Membranes of these materials are not in the state of mechanical stress in fabrication process, and are not exposed to significant deformations during their heating to high temperatures and subsequent cooling. It is explained by proximity of values of their coefficients of thermal expansion to silicon. Furthermore, such membranes are characterized by elasticity. Also, such films are characterized by resistance to etching on the final stage of anisotropic etching of silicon. For the films with lower nitrogen content and higher oxygen content, such as shown in Table 1 under points 1, 2, 3 and 4, characterized by the constant state of mechanical stress. At manufacturing, when the substrates were removing from the hot etchant, some of such membranes are destructed. It was led to rejection of the entire substrate. Also, such films are not characterized by resistance to etching on the final stage of anisotropic etching of silicon. Also at mechanical stresses in membranes the significant effect provides

thermal silicon oxide underlay. The formation of membrane films on silicon substrates without thermal silicon oxide underlay does not provide required level of film adhesion to substrate surface. The admissible thickness of thermal silicon oxide underlay for manufacturing of dielectric membrane structures for sensitive elements of semiconductor gas sensors was experimentally found and amounted of about 100 nm. For obtained silicon oxynitride membranes with the thickness of about 2–3 μm the thermal silicon oxide underlay of such thickness does not contribute to occurrence of critical mechanical stresses during their fabrication and heating.

4. Conclusions

In the modeling was revealed that the membranes of silicon oxide provides the best heat insulation properties, but the membranes of silicon nitride and four-layer membranes provides fast stabilization of temperature at heating and quick output mode to measurement temperature of gas concentration. Four-layer films possess better heat insulation properties of sensitive layers, which is their advantage over the membranes of silicon nitride.

For the membranes based on the films with high oxygen content and on the films obtained on the thick thermal silicon oxide underlayer the heating process was accompanied by "crackling". It was indicated about destructions of the interface substrate - dielectric film. Thus, the optimal gas flow into reaction chamber during the formation of the dielectric membrane films by reactive magnetron sputtering of silicon in the environment of argon, nitrogen and oxygen is: $Q(\text{Ar}) = 1.2 \text{ l/h}$, $Q(\text{O}_2) = 0.2 \text{ l/h}$, $Q(\text{N}_2) = 3.6 \text{ l/h}$. This mode allows to get the films with close elemental ratio to: $\text{Si}:\text{O}:\text{N} = 2:1:1$. Also, such films characterized by resistance to etching in solution: ethylenediamine; pyrocatechol; water = 55%; 20%; 25% (mass fraction of the etchant components). The optimal thickness of the thermal silicon oxide underlayer for formation of silicon oxynitride membranes with the thickness of about 2–3 μm is 100 nm.

References

- Sakai, G., Baik, N., Miura, N., Yamazoe, N., 2001. Gas sensing properties of tin oxide thin films fabricated from hydrothermally heated nanoparticles. *Sensors & Actuators B* 77, 116–121.
- Heule, M., Gauckler, L.J., 2003. Miniaturised arrays of tin oxide gas sensors on single microhotplate substrates fabricated by micromolding in capillaries. *Sensors & Actuators B* 93, 100–106.
- Miasnikov, I.A., Suharev, V.Ya., Kupriyanov, L.Yu., 1991. Semiconductor sensors in physico-chemical studies. Maik Nauka; Moscow, pp. 327.
- Obvintseva, L.A., 2008. Metal oxide semiconductor sensors to detect reactive gases in the air. *Mendeleev Russian Chemical Society* 52, 113–121.
- Bubnov, Yu., Golikov, A., Kazak, A., 2008. Semiconductor gas sensors and gas analysis instruments based on them. *Journal of Electronics: Science, Technology, Business, Special Issue: 72–76*.
- Kozlov, A.G., 2006. Thermal microsensors: classification, the main types. *Journal Nano- & Microsystem Engineering* 4, 2–13.
- Kozlov, A.G., 2008. Thermal microsensors: design features. *Journal Nano- & Microsystem Engineering* 1, 16–28.
- Iovdalsky, V.A., Olihov, I.M., Bleyvas, I.M., 1996. Hybrid integrated circuit gas sensor. R.F. Patent 2,137,117.
- Maccagnani, P., Dori, L., Negrini, P., 1999. Thermo-insulated microstructures based on thick porous silicon membranes. *Proceedings of Eurosensors XIII. Hague, Netherlands*, 817–820.
- Gogish-Klushin, S.Yu., Gogish-Klushina, O.S., Elchanin, A.V., 2010. Features of the behaviour of semiconductor gas sensor film type when operating in power saving mode. *International scientific journal for alternative energy and ecology* 7(87), 18–22.
- Vasiliev, A.A., Gogish-Klushin, S.Yu., Gogish-Klushina, O.S., 2006. Gas sensors with thin membranes of nanocrystalline alumina as sensing elements. *Sensors & Systems* 10, 4–8.
- Heater, M., Graf, M., Taschini, S., 2003. Integrated metal-oxide microsensor array of micro-hotplates with MOS-Transistor. *Proceedings of Eurosensors XVII. Guimaraes, Portugal*, 661.
- Puigcorbe, J., Vila, A., Gracia, I., 2001. Dielectric micro-hotplate for integrated sensors: an electro-thermomechanical analysis. *Proceedings of Eurosensors XV. Munich, Germany*, 312–315.
- Guillemet, J.P., Astie, S., Gué, A.M., 2000. Design of a low power SnO_2 gas sensor integrated on silicon oxynitride membrane. *Sensors & Actuators B* 67, 84–88.
- Veselov, D.S., Voronov, Yu.A., Voronov, S.A., 2011. Technology for producing dielectric membrane structures for integrated gas-sensitive sensors. *Sensors & Systems* 7, 38–42.
- Veselov, D.S., Voronov, Yu.A., Voronov, S.A., Orlova, L.K., 2012. Method for manufacturing multipurpose gas composition sensors. R.F. Patent 2,449,412.
- Veselov, D.S., Voronov, Yu.A., Voronov, S.A., 2013. Sorption gas sensors based on dielectric membrane structure. *Nuclear Physics and Engineering* 1, 10–16.
- Veselov, D.S., Voronov, Yu. A., Vanjuhin, K. D., 2015. Organic alkalis application for manufacturing of MEMS-structures gas sensors. *Sensors & Systems* 1, 45–49.